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**Third Quarterly Technical Progress Report on
Development and Testing of Electrolyte Matrix
Combinations for Mercury-Potassium Fuel Cell
(12 June—12 September 1963)**

NASA CR 52141

Engineering Department Report No. 3609

NASA Contract NASw-476

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Development and Testing of Electrolyte Matrix
Combinations for Mercury-Potassium Fuel Cell²⁺

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I. INTRODUCTION

This is the third quarterly technical progress report on development and testing of electrolyte matrix combinations for mercury-potassium fuel cell for the period 12 June—12 September 1963. This work is being conducted under NASA Contract NASw-476.

Further work with fine MgO powder led to the eventual improvement of the KOH-KBr-KI eutectic-MgO composite. Two major changes are (1) the use of a new packed-baking process, and (2) the use of a new grade MgO. The results of six small cell tests, conducted during this period, contributed to the composite development program. All tests showed that the matrix cracked at some stage of operation. The sixth test gave over 12 hours of performance under a limited operating condition.

Improvement of performance by the use of the fine grain material, as was predicted by results of conductivity measurements on these composites, has been demonstrated by these tests. Further work in the last quarter will emphasize cell tests using state-of-the-art fabrication techniques for the composite matrix. Considerable effort will be devoted to cell construction, assembly, and loading techniques to give the highest degree of reliability to the testing program. Large cells will be constructed and tested after small cell work verifies design feasibility.



II. SMALL LMC OPERATION

Six tests were accomplished during the period. Discussion of each test is given in the following paragraphs along with the data tables. The cells have been designated by the initials NASA followed by Roman numerals. The first two, NASA-I and NASA-II, were reported in Allison EDR 3455. This report discusses cells NASA-III through NASA-VIII.

NASA-III

The first cell, NASA-III, was assembled with a nominal 34% electrolyte composite matrix. The material had been estimated to be near an optimum strength value between 33% and 35%. However, the analyzed value was found to be near 35% and the strength tested out to correspond with that for 35% electrolyte composites.

Cell testing was accomplished by adding K-metal to the anode side where it became saturated with a preloaded electrolyte. This retards a direct attack on the matrix. The voltage potential between the K-metal and the Hg vapor deposit from the preheater attained 1.23 volts but showed an unstable shorting from the start. An electrical load check proved the potential to be caused by a high resistance cell, greater than 4 ohms. Internal shorting eventually reduced the potential to near zero.

The test was continued by adding Hg to the cathode side. A low resistance K-Hg cell was formed, momentarily, with a potential of 0.97 volts. However, a dead short reduced this value to zero with a rise in temperature caused from direct reaction between the anode and cathode metals.

Posttest analysis showed that the seal region of the composite held up without leakage. The cause of failure was attributed to the rupture of the weak matrix which indicated need for a mechanical support in future testing. A recommended rerun of the test using a nominal 33% electrolyte composite became cell NASA-IV.

NASA-IV

NASA-IV was operated to test a newly prepared composite from the coarse grain MgO. The material was prepared by new techniques to minimize moisture. Analysis results show the electrolyte content to be very nearly 33% and the percent of theoretical density to be 82%. This test also was accomplished without the use of mechanical support for the matrix since the strength of the material had been shown to resist deformation (NASA-I, Second Quarterly Report).



The test was started by the addition of K-metal to the anode side while Hg was in the preheater below the cathode chamber. The initial potential voltage was recorded at 0.3 volts but then was discovered to be that of a loaded cell with a current approximately 80 ma. Instantaneous open circuit recovery to 0.82 volts at 90 ma gave a cell resistance computed as 1.05 ohms. This was subsequently measured as 2.00 ohms and 1.4 ohms prior to shorting. The performance is indicative of a high resistance cell prior to filling with Hg on the cathode side. The early performance served as an indication of cell stability. In this case, however, a dead short dropped the voltage to zero before the cathode chamber was filled with Hg.

Recovery of the cell with the introduction of Hg was unstable. The open circuit potential reached 0.80 volts, and 250 ma current was drawn momentarily. This cell appeared to develop an internal short which depressed the terminal voltage to nearly zero. Attempts to recharge the cell failed.

Cell testing of coarse MgO composites showed some degree of success to this point in the program. Posttest analysis showed that the concentric-serrated seal does function throughout the test. In general, the cause of failure has been due to very fine cracks in the completed matrix.

The development of the fine grain MgO composites (described in another section of this report) has gone slowly. Work has been hampered by the difficulty of producing sound, stress-free specimens. After one composite broke during cell assembly, a "green" specimen was used in an attempt to process the matrix within the cell housing prior to the loading of electrode metals. In this way, thermal cycling was eliminated. This configuration became cell NASA-V.

NASA-V

The "green" specimen was placed in the cell and care taken not to close the cell halves before the composite baked out. During this part of the procedure, the cell was in the horizontal position. The cell was rotated to the vertical position the following day in preparation for the test. The initial Hg loading indicated that the matrix was not sound. Further Hg filling showed that the cell chambers were electrically shorted (zero resistance). Also, Hg was detected in the anode side. Posttest analysis showed that the matrix had ripped apart at the cell opening and seal edge. This damage was caused by shrinkage of the middle of the matrix while the seal serrations held the outer perimeter material.

A new generation of fine grain composites was developed using an MgO powder reported to be a high purity fused product. The grain size was measured to be from 0.04 to 0.10 micron with the predominant sizes in the 0.07 to 0.09 micron range. A further change in processing



was that of vacuum-packed baking which is described in the third section of this report. X-ray analysis showed these materials to be greatly improved over those from earlier batches. Three cells were operated to test this new material.

NASA-VI

Cell NASA-VI was assembled using a composite which was made up as nominal 56% electrolyte. Analysis shows that this material changes to approximately 53% electrolyte content through desaturation during the baking process. The theoretical density was measured as 86.2%.

This cell was fabricated with a set of temporary stainless steel screens inserted on each side of the matrix. A change in cell operating procedure was also incorporated in the formation of this cell. Hg was loaded into the cathode chamber through the preheater prior to K-metal loading. While in this condition, a slight potential was detected from a very high resistant cell. This potential, near a quarter volt, was useful as a shorting indicator. In this cell, it indicated that the matrix was holding under a head of Hg from the cathode side.

Introduction of K-metal to the anode chamber caused the potential to rise to 1.28 volts. However, unstable performance began within 5 minutes. Electrical loading to gain specific performance values was limited by the unstable operation which dropped the open circuit voltage to zero within 10 minutes.

Subsequent attempts to recharge the cell proved that the cell was dead. Posttest analysis again showed that the composite possesses good strength and sealing characteristics, but very fine cracks allowed K-metal to penetrate to the cathode and short the cell.

NASA-VII

The seventh cell, NASA-VII, was assembled with another matrix prepared from the same material as that for NASA-VI. The density of this composite was 85.5% of theoretical. The initial voltage after Hg loading was 0.39 volts but dropped off to 0.10 volts when the Hg made contact with the matrix. Although this early indicator voltage dropped, no unstable operation was apparent and K-metal was introduced into the anode.

The full cell potential of 1.34 volts was realized on this cell. However, this occurred as a peak value for about 0.2 min and then shorted to 0.14 volts. Charging current failed to hold the cell and it was dead within 4 min. Failure analysis showed once again that fine cracks caused the electrical short through K-metal contact.



An effort to reduce cracks and/or repair them by a self-healing process led to the new highly saturated matrix. This specimen was prepared from a nominal 65% (analyzed as 64.8%) electrolyte content composite and pressed to a high density (93%). Operation of this matrix was accomplished in cell NASA-VIII.

NASA-VIII

Permanent supporting stainless steel screen was used for this cell. The rework caused the cell area to increase to 6.4 cm^2 from the 5.1 cm^2 , reducing the seal area.

Care was taken to check each procedure of cell formation and operation for an adequate time to determine its contribution to failures. The matrix was placed in the cell and heated to 300°C over a six-hour period. The tightening sequence to close the cell and form the seal was prolonged over an hour period. The cell remained in this condition overnight.

The next morning a potential of 0.60 volts had developed across the cell halves. A check of the resistance by electrical loading proved this to be stray or residual and of no consequence to cell operation. The addition of Hg to the preheater caused a reduction in this voltage.

Hg was loaded into the cathode chamber to full capacity and allowed to set for $2 \frac{1}{2}$ hr. The residual voltage used as an indication of matrix condition changed only slightly and slowly during this time. Since 0.16 volts still remained at the end of this time it was assured that no shorting had occurred.

A change in procedure for K-metal loading called for loading to be accomplished in small increments over the day. The first five grams proved to be adequate. These five grams of K-metal gave a potential to the cell for over 12 hours. Only limited power operation was accomplished during this time.

The initial voltage was a typical 1.35 volts for K-Hg cells. Subsequent electrical testing gave resistance values in the range of 0.15 to 0.20 ohms. These correspond to resistivity values of 3.0 to 4.0 ohm-cm for the matrix with an area of 6.4 cm^2 and thickness of 0.32 cm. These values are in line with those predicted for this type electrolyte matrix.

Posttest analysis shows that this matrix had cracks. There was a clear region near the bottom where the K-metal made contact and produced a cell without early shorting. Apparently it was only a matter of time for these cracks to fill with K-metal or amalgam and cause an internal current leak path.



A review of progress to this point indicated the need for increased effort in reducing and/or repairing cracks in the composite matrix. It was not determined as to when in the process these cracks occurred. Nevertheless it was determined that high internal stresses are set up in the specimen during thermal cycling of the bake and cool-down procedures. Subsequent heat-up within the cell may cause damage if not heated slowly. Also, sudden chilling by the introduction of liquid metal could cause failures. It may be possible that the high activity of the pure potassium is a severe condition to impose on the nonsaturated molten salt which binds the composite through capillary forces.

In consideration of these concepts a new program emphasizing cell testing techniques will follow. The ultimate goal remains, the testing of two 3-in. diameter cells. However, these tests are dependent upon the success of the small cell work.



Table I.

Data on composite electrolyte matrix cells.

Cell, electrolyte percentage, and date	Time of day	Cell potential V_o^* (volts)	Cell voltage under load V_c (volt)	Load current, I (amp)	Computed cell resistance R (ohms) ¹	Resistivity γ (ohm-cm)
NASA-III 34% 7-5-63	2:17	0.97				
	2:19	1.23				
	2:30	1.10 (Unstable)				
	2:33	0.80	0.32	0.12	4.0	—
	2:34	0.98 (Unstable)				
	2:36	(Heavy internal short)				
	3:16	0.25	(Load Hg)			
	3:17	0.80				
	3:18	0.97				
		(Dead short—no recovery)				
NASA-IV 33% 7-24-63	1:33		0.3	~0.08		
	1:34		0.5	~0.08		
	1:37	0.82	0.735	0.09	1.05	—
	1:40	0.97	0.85	~0.06	~2.00	—
	1:48	1.00				
	1:58	1.02				
	1:59	0.10	(Sudden short)			
	2:04	0.00				
	2:07	(Load Hg)				
	2:08	~0.25				
	2:10	0.80				
	2:12	—	0.80	0.25		
	2:13	0.20				
	2:14	0.12				
		(Charging 0.6 to 0.9 amps)				
NASA-V (Green) 8-9-63	4:11	0.02	(Dead)			
		(No performance data)				
NASA-VI 53% 8-15-63	8:55	(Cell in vertical position)				
	9:15	0.24	(Hg into preheater)			
	1:38	0.24	(Start Hg fill)			
	1:50	0.26	(Finish Hg fill)			
	2:06	> 1.00	(K-metal load)			
	2:07	1.20				
	2:10	1.28				
	2:12	1.22	(Unstable)			
	2:13	—	1.02	0.07		
	2:14	—	1.02	0.07		
	2:15	—	0.95	—		
	2:16	0.79	(Open circuit)			
	2:17	0.24				



Cell, electrolyte percentage, and date	Time of day	Cell potential V_o^* (volts)	Cell voltage under load V_c (volt)	Load current, I (amp)	Computed cell resistance R (ohms) ¹	Resistivity γ (ohm-cm)
NASA-VII 53% 8-28-63	2:18	0.11				
	2:19	0.04				
	2:20	0.02				
	2:21	0.02				
		(Charging)				
	3:15	0.01				
	8:20	0.39	(Hg loaded to preheater)			
	8:30	0.33				
	8:55	0.10	(Hg filled to contact matrix)			
	9:03	0.08	(Hg full)			
	9:05	0.06	(K-loading started)			
	9:09	0.08				
	9:10	0.14	(K contact)			
	9:10	1.20	(Step rise)			
	9:10:24	1.34				
	9:10:36	0.14				
	9:11	—	0.16	0.80	(Charging)	
	9:15	—	0.05	0.80		
	9:15+	0.00				
NASA-VIII 65% 9-12-63	9:02	0.6	(Without LM's)			
	9:44	0.49	~0	~0	High	
	9:52	0.48	(Voltage recovery)			
		(Add Hg to preheat)				
	10:30	0.35				
	10:40	0.29	(Hg filled)			
	1:02	0.16				
		(Add 5 grams K-metal)				
	1:09	1.20				
	1:10	1.30				
	1:13	1.34				
	1:15	1.35				
	1:32	1.35				
	1:35	1.34	(Slightly unstable)			
	1:53	1.23	(Unstable)			
		(Electrical load)				
	1:56	1.11*	1.02	0.60	0.15	3.0
	1:59	1.15				
	2:05	—	0.90	0.90	—	—
	2:09	0.87*	0.72	0.75	0.20	4.0
	3:31	0.87				
		(Charging)				
	3:44	1.05	1.13	0.48	0.167	3.34
	3:49	—	—	0.45	—	—
	3:57	0.74*	0.68	0.37	0.162	3.24
	4:17	0.80				
		(Charging)				
	4:40	0.935				
	6:00	0.83				
	7:00	0.83				



<u>Cell, electrolyte percentage, and date</u>	<u>Time of day</u>	<u>Cell potential V_o^* (volts)</u>	<u>Cell voltage under load V_c (volt)</u>	<u>Load current, I (amp)</u>	<u>Computed cell resistance R (ohms)¹</u>	<u>Resistivity γ (ohm-cm)</u>
	8:00	0.81				
	9:00	0.78				
	10:00	0.72				
	10:30	0.69				
	11:00	0.40				
	11:30	0.09				
	12:00	0.07				
	1:00	0.16				
	2:00	0.17	(Lost recording marker)			

¹ Cell resistance is computed from an instantaneous cell potential to eliminate the effect of electrode concentration gradients. This technique is described in Figure 13 of the First Quarterly Technical Progress Report, Allison EDR 3277, and is given as

$$R_c = \frac{V_o^* - V_c}{I}$$



III. IMPROVEMENT AND FABRICATION OF COMPOSITES

Early work with the fine grain MgO was reported in the Second Quarterly Progress Report, Allison EDR 3455. The fabrication of the three composites with electrolyte contents of 55, 57.5, and 60% was made to begin the search for optimum properties. Data on conductivity, strength, and flowability was tabulated for these composites. Since then, batches have been designated by century numbers beginning with 101 and are shown in Table II along with all recent composites.

Composites are identified by a nominal electrolyte-to-MgO weight ratio and a percent electrolyte content as determined from chemical analysis. More emphasis was placed on the improvement of the quality of composites and less on testing for properties. Therefore, only spot-check data are shown for strength and flowability.

The first three batches of composite proved to be unsatisfactory for the fabrication of 2-in. x 1/8 in. disks for use in liquid metal cell testing. In all cases cracks and/or blisters formed during the processing.

Batch 104 was processed from a newly prepared KOH-KBr-KI eutectic. A 2-in. x 1/8-in. disk which did not show visible cracks or blisters was fabricated from this material. Subsequent X-ray examination revealed fissures or discontinuities.

A considerable amount of time was spent in establishing a valid X-ray technique for analysis. Several specimens with varying degrees of visible fissures and flaws, and several not exhibiting such flaws, were subjected to variable X-ray techniques to find a suitable set of parameters. These parameters are: 140 kv, 5 ma, no filter, 15-sec exposure for 1/8-in. specimens and 120-sec for 1/2-in. specimens, focal distance 40-in. Eastman AA film, and cardboard holders. All specimens are now given an X-ray check before use in cells.

In order to X-ray the specimens without exposure to air they were first packaged in plastic bags. Later it was determined that these bags were not adequate protection over long periods of time in storage. Holders were constructed of 1/4-in. plexiglass sheets, and separated and sealed by rubber O-rings. These holders were tested and proved gas tight. This provides a method for preserving all specimens while being X-rayed, photographed, and stored for long periods.

A critical review of the fabrication technique ensued. At this time the procedure was changed to include the use of an argon flooding cabinet to handle all steps which were previously done in air. This then eliminated the chance of H₂O or CO₂ contaminating the mixtures.



After these precautions were taken the next three batches, 105, 106, and 107, were prepared. These composites represent a second look at the overall range of electrolyte-MgO ratio in view of the recent improvements. Batch 105 with 70% electrolyte proved to be oversaturated and could not exist at cell operating temperature. Batch 106 with 50% electrolyte gave the best indication of crack-free quality but appeared too dry and crumbled easily at the cell operating temperature. Batch 107 with 60% electrolyte displayed properties much like those for batches 103 and 104. Cracking and blistering still hampered the fabrication program.

Effort continued to find a composition and/or a fabrication technique which would produce crack- and blister-free specimens. Batches 108 and 109 contributed property data which fell in line with other work, but with the same poor quality.

Two batches, 110 and 111, were prepared at a nominal 56% electrolyte content. Batch 110 used a new fine grain MgO which was classified as an electronic grade and thought to be a fused material. The other batch, 111, was prepared from the old material which is now known to be a light calcined MgO. Early attempts to fabricate 2-in. x 1/8-in. disks from these batches, indicated that the old material gave the better quality. Processing techniques used later proved the electronic grade to be superior in quality.

All baking processes to this point in the program had been accomplished on a metal support. The two materials used were nickel and gold. The problem with this technique lies in the nonuniform surface pressure and temperature on the specimen. This was generally conceded to be the cause of warping. After a complete study of baking procedures, including the use of thin foil, an entirely new baking environment was tried.

This technique makes use of the coarse grain MgO (5μ average) as a packing material for the fine grain, "green," cold-pressed composite. In this configuration, the specimen has a uniform environment. Specimens which have been baked in this manner, under a vacuum and with use of slow heating and cooling rates (10°F/hr), have shown the best quality yet attained.

One drawback to this procedure, and the first objection to it at its inception, is the fact that desaturation of the specimen through loss of electrolyte to the packing material is possible. Table II, for Batch 110, shows a loss reflected in the difference between nominal value and analyzed value of electrolyte content. However, a later batch, 112, does not show this tendency, and it is now known to be a minimum.

The latest techniques in the preparation of KOH-KBr-KI eutectic-MgO composite electrolyte is now considered as state of the art. This has been done to gain control of variables in cell testing. Batch 112 represents a highly saturated matrix called for in cell



testing with use of supporting screens. Other batches will be made to fixed specifications as the cell testing program continues. Work in the fabrication of large (4-in. x 1/8-in.) disks is now being carried out in the composite development program.



Table II.

Fine grain MgO composite, identification, and properties.

Batch no.	Nominal weight ratio	Analyzed electrolyte content %	Percent of theoretical density	Temperature 300°C	
				Ball penetration strength (psi)	Flowability % deformation
101	55/45	55.0	—	2.5	10
102	57.5/42.5	56.4	—	1.9	13
103	60/40	61.2	—	1.9	12
104	63/37	63.0	90	2.5	19.7
105	70/30	69.3	73	—	(Fluid)
106	50/50	52.5	88	22.0	3.5
107	60/40	61.7	90	2.6	17.5
108	55/45	55.5	87	15.2	9.4
109	58/42	58.2	88	1.5	11.0
110*	56/44	52.8	89	5.7	16.8
111	56/44	56.7	91	10	11.7
112*	65/35	64.8	87	4.3	20.5

*Electronic grade fine MgO used.